

Rare-earth Information Center INSIGHT

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Active Fluoride Glasses

As reported earlier (RIC Insight 1 [3] (1988) and 4 [7] (1991)) rare earth-heavy metal fluoride glasses are seriously being studied for long distance telecommunication systems to replace silica based systems, because the fluoride glasses have a low loss window, i.e. are transparent, at longer wavelengths than the silica glasses (2.55 vs. 1.55 μm) and have a lower intrinsic (theoretical) loss (0.01 vs. 0.15 dB/km). The first allows one to send more information per fiber, and the second allows one to transmit this information over longer distances without amplifying the signal (150 km vs. But to date there has been some difficulty in reaching these goals for the fluoride glasses, which require purity levels of transition and lanthanide elements, which absorb in the visible and infrared regions, to be less than 1 part per billion. Furthermore, extrinsic scattering loss factors, such as bubbles and microcrystallites, need to be eliminated or reduced to an extremely low level. To date the best that has been achieved is a loss of 0.6 dB/km for a 110 m long wire, about a factor of 50 too large to be useful in long distance telecommunications.

At the 19th RERC Prof. J. Lucas (Laboratoire de Chimie Minerale, Université de Rennes, France) described a new and interesting development, involving rare earth fluoride glasses, which may reach commerical fruition much sooner than optical fibers for transmission lines. Scientists have found that the lanthanide doped fluoride fibers have a unique guiding configuration which allows these materials to be used as optical amplifiers and fiber lasers. The lanthanides, which are homogeneously distributed in the core of the fiber, can easily be excited by pumping light into the fiber and guiding the emitted beam through the fiber core. The high optical confinement results in a highly efficient optical excitation, leading to a low power threshold for laser action or up-conversion processes. Since the optical fiber is quite short -- a few meters in length -- optical losses of 0.5 to 1 db/km can be tolerated. These rare earth doped waveguides are called rare earth active fluoride fibers to distinguish them from the classical optical fibers.

There are three fluoride glasses which are primary candidates for active fibers. All three have been drawn into the fibers and shown to be stable enough to resist corrosion and devitrification. These are: ZBLAN, an AlF3based glass, and BIGaZYT. ZBLAN is a fluorozirconate glass having the composition 55ZrF4-18BaF2-6LaF3-4AlF3-17NaF. This is the most stable fluoride glass known today (i.e. it has the lowest critical cooling rate),

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but its high NaF content makes it susceptible to water corrosion. But as noted in the July 1, 1991 issue of RIC Insight, the Japanese have developed a process to form an oxyfluoride coating on the surface which protects the ZBLAN from water corrosion. The fluoroaluminate glass, which contains Al,Zn,Y,Sr and Na has excellent chemical durability, but its absorption edge is a little lower than that of ZBLAN. BIGAZYT glass contains Ba,In,Ga,Zn,Yb and Th fluorides and has the major advantage that its IR (infrared) edge is around 8 μm significantly larger than of ZBLAN, however, its absorption is higher than the other glasses below 3.5 μm . But in active fibers because of short distances this is not a major problem.

In all these applications the rare earth fluoride is not one of the major components, but they are always present because they are glass stabilizers and contribute to the formation of the glass framework. For this reason lanthanide fluoride dopants are easily dissolved, and this is important for these new developments which utilize the lanthanides at fairly low concentration levels (100 to 1000 ppm) as activator ions. It also turns out that radiative (laser) emissions are more efficient in the fluoride glasses than other host materials, and a large number of laser transitions have been demonstrated in lanthanide doped fluoride glasses. Thus with a variety of different lanthanide ions a fairly complete range of laser wavelengths, ranging from 0.45 $\mu\mathrm{m}$ in the visible up to 2.9 $\mu\mathrm{m}$ in the infrared, have been identified. The major laser lanthanide ions studied include Nd³+, Ho³+, Er³+ and Tm³+. One can expect in the near future the use of lanthanide-doped fluoride fibers as compact and efficient visible radiation sources by using semiconductor laser diodes as the optical pump.

The use of these lanthanide-doped fluoride glasses as optical amplifiers is another important new development which is near commercialization. A Nd³+-doped optical fiber, which was pumped by a 820 nm semiconductor laser, achieved a 10 dB gain at a wavelength of 1.343 μm . Because of excited-state absorption by the silica glass, the silica-based optical amplifiers are not available at the 1.343 μm wavelength. An even higher gain (20 dB) has been achieved for Er³+ doped fluoride glass at 1.55 μm using a laser diode pump at 1.48 μm . Other possible applications include: optical recording; medical and optical sensors; thermal imaging; and chemical sensors for monitoring pollution, and for emission and reaction controls.

Largest YAG Single Crystal

Sumitomo Metal Mining Co., Ltd. has developed an improved process for making the largest commercially available YAG (yttrium aluminum garnet) single crystals. These crystals are 25 cm long and 12.5 cm in diameter, which compares to the previous record material of 20 cm long by 6 cm in diameter. The crystals are doped with ~1% Nd and can be formed into rods or slabs. These enlarged single crystals makes it possible to increase the laser output to several gigawatts (109 watts) and thus makes these YAG:Nd lasers competitive with CO2 gas lasers for metal processing.

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